

GEOCHEMICAL VARIATION OF INORGANIC CONSTITUENTS IN A NORTH DAKOTA LIGNITE

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INTRODUCTION

This paper summarizes information on the distribution of major and trace elements in a stratigraphic sequence of sedimentary materials in a major lignite producing portion of the Fort Union region of the Northern Great Plains. Previous study of the geochemical variation in these sediments is summarized in the literature (1,2). Major patterns of elemental variations in lignite are related to factors affecting accumulation of both organic and inorganic components during deposition and aqueous precipitation, dissolution, and ion-exchange processes after deposition. Variations in overburden and underclay are dependent upon specific clay mineral variation and relative abundances of quartz- and feldspar-rich silt fractions versus clay mineral-rich fractions of the sediment, as well as upon local variation in carbonates and other elements.

GEOLOGIC RELATIONSHIPS

The Center mine, Oliver County, North Dakota is in the Fort Union Coal Region, which is one of the largest reserves of lignite in the world. The Fort Union Coal Region lies within the North Great Plains Coal Province and encompasses portions of north-central United States and south-central Canada, including both the subbituminous coals of the northern Powder River Basin and the lignites of the Williston Basin (2), a broad structural and sedimentary intracratonic basin that extends over an area of about 40,000 km². Over 4600 m of sedimentary rocks overlie the Williston Basin in its deepest portions of McKenzie County, North Dakota.

Important lignite beds of the Fort Union Region occur within Ludlow, Slope, Bullion Creek, and Sentinel Butte Formations of the Paleocene Fort Union Group.

The Sentinel Butte Formation has been described as a "lignite-bearing, nonmarine, Paleocene unit whose outcrops are somber gray and brown" (3). Rock types include sandstone, siltstone, claystone, lignite, and limestone. The lignite beds typically vary from less than 1 meter to 3-5 meters in thickness (4). The Oliver-Mercer County district is located in eastern Mercer and northeastern Oliver Counties with the principal bed, the Hagel bed, ranging in thickness from 3 to 4 meters at the Center Mine (4).

The sampling program (5) was designed to obtain stratigraphically controlled specimens for a study of the character, distribution, and origin of the inorganic constituents in lignite. The objectives of the field sampling were to obtain:

1. Incremental samples of underclay, lignite, and overburden at each mine.
2. Duplicate vertical sections and lateral samples to test variation.
3. Samples of specific beds, lenses, fault zones, mineral concentrations, or other areas of unusual aspect.

Lignite, lignite overburden, and underclay were collected from a vertical section on the high walls at the Center mine. Figure 1 illustrates the stratigraphic sections and sample locations. Choice of sections to be sampled was based on accessibility to areas in the mines due to mining activity.

To minimize contamination, material from slope wash and mining activity was first removed from each section. In order to obtain samples of underclay it was necessary to dig down at the base of the lowest lignite, since in surface mining the underclay is normally left undisturbed. Once the section to be sampled was exposed it was measured and marked at 30 cm intervals (through the lignite, starting at the base) and then at additive increments of 1 m through the extent of the overburden in the mine cut.

Samples were collected (Table 1) over a 10 cm by 50 cm area at the bottom of each marked interval of the measured section. Samples were collected at all contacts between lithologic units when the contact was found and at points of interest (for example: iron sulfide-coated joints, clay partings, sand lenses, concretions). All samples were stored in plastic bags inside cardboard cartons.

TABLE 1
SAMPLE DESCRIPTIONS AND LOCATION, CENTER MINE

| <u>Sample #</u> | <u>Height, meters*</u> | <u>Description</u> |
|-----------------|----------------------------|--|
| 1-1-D | -0.05 | Underclay, gray |
| 1-2-D | 0.05 | Black lignite, very hard |
| 1-3-D | 0.40 | Black lignite, very hard |
| 1-4-D | 0.70 | Black lignite, very hard |
| 1-5-D | 1.00 | Black lignite, very hard |
| 1-6-D | 1.25 | Black lignite, very hard |
| 1-7-D | 1.50 | Black lignite, very hard |
| 1-8-D | 1.70 | Black lignite, very hard |
| 1-9-D | 1.90 | Black lignite, very hard |
| 1-10-D | 2.10 | Black lignite, very hard |
| 1-11-D | 2.45 | Black-brown lignite, soft and fractured, top of seam |
| 1-12-D | 2.55 | Dark gray organic rich silt |
| 1-13-D | 3.65 | Gray sand, fine-grained, fossilized |
| 1-14-D | 4.15 | Gray sand with a clay matrix |
| 1-15-D | 4.50 | Concretion zone |
| 1-16-D | 4.75 | Brown lignite, very soft, silty |
| 1-17-D | 4.85 | Gray-green clay |
| 1-18-D | 5.15 | Brown lignite, very soft, silty |
| 1-19-D | 5.45 | Brown lignite, top of seam |
| 1-20-D | 5.60 | Gray silty clay |
| 1-21-D | 5.75 | Brown lignite with silty interbedded layers |
| 1-22-D | 5.85 | Gray siltstone |
| 1-23-D | 6.45 | Gray siltstone, 1-2 mm laminae |

*Height from base of major lignite seam.

GEOLOGICAL CHARACTERISTICS

The Center mine lignite is a black to brownish black coal that slacks rapidly on exposure to the atmosphere and typically contains dark carbonaceous clay or grey clay partings (4). The underclay is a grey-green clay with lignite fragments. The overburden is grey fine-grained sediment primarily consisting of clayey silts and silty clays with minor concretionary zones and sands. Logan (6) has described the overburden sequence as the Kinneman Creek interval and has interpreted it to be of lacustrine origin. Generally the early Cenozoic sediments in this region are believed to have been deposited in a coastal complex of stream channel and flood plain, swamp, lake, and delta environment.

INORGANIC CONSTITUENTS

Inorganic constituents in the Sentinel Butte sediments are present as 1) detrital mineral grains and volcanic glass fragments, 2) components of organic debris, 3) authigenic mineral grains and cement, and 4) ions adsorbed by clay and other minerals and organic material (7,8,9,10).

A summary of minerals observed in the Sentinel Butte Formation is given in Table 2 (9). Major original detrital constituents include montmorillonite, quartz, plagioclase, alkali feldspar, biotite, chlorite, volcanic glass and rock fragments. Major minerals formed during deposition and diagenesis by conversion of original detrital constituents consist of montmorillonite, chlorite, and kaolinite. Pyrite, gypsum, hematite, siderite, and calcite (?) formed in post-depositional reducing and oxidizing reactions related to changing conditions of deposition, burial, and ground-water movements.

TABLE 2
INORGANIC CONSTITUENTS IN THE SENTINEL BUTTE FORMATION

| <u>Constituent</u> | <u>Overburden</u> | <u>Lignite</u> | <u>Underclay</u> |
|--------------------|-------------------|----------------|------------------|
| Alkali feldspars | XX | X | X |
| Augite | | X | |
| Barite | | X | |
| Biotite | X | | |
| Calcite/Dolomite | XX | X | |
| Siderite | XX | | |
| Chlorite | XX | X | X |
| Gypsum | | XXX | |
| Hematite | | XX | |
| Hornblende | X | | |
| Illite | XX | X | X |
| Kaolinite | XX | XXX | XXX |
| Magnetite | X | | |
| Montmorillonite | XXX | X | XXX |
| Muscovite | X | | |
| Plagioclase | XXX | X | X |
| Pyrite | | XX | |
| Quartz | XXX | XXX | XXX |
| Volcanic Glass | X | | |
| Rock fragments | XX | | |

XXX = Abundant

XX = Common

X = Minor

GEOCHEMICAL VARIATION IN OVERBURDEN AND UNDERCLAY

Previous work (7,8) and our current work seeks to relate chemical variations to variations in the original mineral content of the sediments and to variations due to post-depositional mineral reactions.

Overburden sediments are typically silty clays with about 80 pct clay and 20 pct silt. Other sediments include clayey silts and fine sands with varying organic content and calcareous cement. Sideritic concretion zones are present. Clay-rich sediments are enriched in some elements particularly Al, Mg, and Ti. Carbonate-rich sediments are enriched in Ca and Fe (concretionary zones). Sodium shows a tendency to increase downward to a high in organic-rich silty clay, above the lignite. Specific beds, including the underclay, are markedly enriched in potassium, possibly related to high mica content.

EXPERIMENTAL

Samples of coal, overburden, and underclay were dried and analyzed by neutron activation (NAA) and x-ray fluorescence analysis (XRF). NAA analysis was performed by the Nuclear Engineering Department, North Carolina State University. The system description and detection limits for coal and coal fly ash are summarized by Weaver (11). XRF was done at GFETC with an energy dispersive x-ray system. Mineralogy of the overburden and underclay was determined by x-ray diffraction (XRD). The crystalline phases present in the coal were determined by XRD of the low-temperature ash of the coal.

RESULTS AND DISCUSSION

Mineralogy of the Stratigraphic Sequence - X-ray diffraction was used to determine the major minerals present in the overburden, underclay, and of the low-temperature ash of the coal. The results are summarized in Figure 2, which illustrates the distribution of minerals throughout the sequence. The most distinct variation in the overburden is the concretion zone, which is a very compact, cemented zone rich in siderite and dolomite. The remaining fractions of the overburden are consistent with varying amounts of quartz, kaolinite, muscovite, and plagioclase.

The bulk mineralogy of the coal also represented in Figure 6 reveals the presence of quartz, calcite, bassonite, kaolinite, and pyrite in varying amounts. Bassonite is possibly a product of organic sulfur fixation with organically bound calcium (12). Pyrite appears to increase with depth in the seam.

Variations of Elements in the Stratigraphic Sequence - The results of the neutron activation and x-ray fluorescence analysis for the stratigraphic sequence are listed in Table 3. Descriptions of the samples are listed in Table 1.

Variation Within Major Coal Seam - The distribution of elements throughout the section sampled in the coal seam can be summarized by four general trends: 1) concentration of elements in the margins; 2) concentration in the lower part of the seam; 3) even distribution; 4) without a clear pattern. These trends can be best examined by plotting or charting them with location in the seam.

The elements which were concentrated at or near the margins of the coal seam included Al, Ti, Fe, Cl, Sc, Cr, Co, Ni, Zn, As, Ru, Ag, Cs, Ba, La, Ce, Sm, and U. An example of a typical distribution is a graph of Zn shown in Figure 3, which illustrates the distribution of zinc throughout the entire stratigraphic sequence.

The elements which are concentrated at the margins of the lignite seam are most likely associated with the detrital constituents, such as finely divided clay min-

TABLE 3
ELEMENTAL ANALYSIS FOR SELECTED MAJOR AND MINOR ELEMENTS, PARTS PER MILLION
(Dry Basis)

| ID | Height* ft. | No. | Mg | Al | K | Ca | Ti | Fe | Cl | Sc | V | Cr | Mn | Co | Ni | Zn | As |
|-------------------|----------------|------|-------|--------|-------|-------|------|--------|-----|----|-----|-----|-----|----|-----|-----|----|
| 1-1-D Underclay | -0.05 | 5332 | 9534 | 95268 | 26788 | 9605 | 4052 | 26761 | 411 | 15 | 137 | 99 | 144 | 5 | 59 | 42 | 4 |
| 1-2-D Lignite | 0.05 | 1518 | 1736 | 10200 | 2153 | 6247 | 724 | 9377 | 132 | 6 | 219 | 49 | 39 | 2 | 34 | 25 | 16 |
| 1-3-D Lignite | 0.40 | 1307 | 1607 | 5586 | 806 | 5984 | 246 | 6685 | 55 | 2 | 25 | 6 | 49 | 2 | 21 | 14 | 20 |
| 1-4-D Lignite | 0.70 | 1398 | 1677 | 2595 | 1000 | 7658 | 119 | 2909 | 44 | 1 | 4 | 2 | 69 | 1 | 16 | 10 | 6 |
| 1-5-D Lignite | 1.00 | 1398 | 1375 | 3313 | 615 | 6888 | 323 | 2326 | 59 | 1 | 22 | 5 | 47 | 1 | 12 | 6 | 6 |
| 1-6-D Lignite | 1.25 | 967 | 1861 | 2949 | 1000 | 6820 | 124 | 1745 | 55 | 1 | 4 | 1 | 68 | 0 | 13 | 8 | 5 |
| 1-7-D Lignite | 1.50 | 1115 | 2209 | 6051 | 1000 | 6994 | 298 | 2182 | 67 | 1 | 16 | 5 | 76 | 1 | 16 | 12 | 8 |
| 1-8-D Lignite | 1.70 | 804 | 827 | 1970 | 1000 | 4689 | 78 | 6128 | 36 | 0 | 1 | 1 | 24 | 1 | 13 | 6 | 31 |
| 1-9-D Lignite | 1.90 | 1006 | 1979 | 10813 | 1104 | 6330 | 357 | 7323 | 74 | 3 | 47 | 10 | 61 | 4 | 28 | 19 | 15 |
| 1-10-D Lignite | 2.10 | 3685 | 9219 | 100370 | 1000 | 8691 | 2578 | 17133 | 407 | 11 | 101 | 68 | 100 | 3 | 33 | 34 | 7 |
| 1-11-D Lignite | 2.45 | 737 | 1848 | 6620 | 1000 | 7935 | 191 | 4070 | 51 | 7 | 12 | 5 | 56 | 1 | 33 | 25 | 21 |
| 1-12-D Overburden | 2.55 | 5814 | 10564 | 79761 | 25718 | 10564 | 3119 | 29506 | 336 | 13 | 138 | 80 | 257 | 11 | 47 | 44 | 8 |
| 1-13-D Overburden | 3.65 | 5331 | 10921 | 71239 | 1000 | 16988 | 3393 | 24822 | 407 | 11 | 116 | 72 | 287 | 11 | 36 | 36 | 3 |
| 1-14-D Overburden | 4.15 | 4461 | 11465 | 95029 | 1000 | 7838 | 3540 | 31466 | 508 | 15 | 170 | 94 | 175 | 15 | 55 | 54 | 3 |
| 1-15-D Overburden | 4.50 | 1422 | 3673 | 96920 | 5000 | 5824 | 4320 | 233070 | 116 | 29 | 138 | 21 | 128 | 1 | 190 | 108 | 2 |
| 1-16-D Lignite | 4.75 | 750 | 1762 | 5813 | 1000 | 6754 | 419 | 28510 | 113 | 15 | 185 | 34 | 66 | 10 | 166 | 40 | 28 |
| 1-17-D Overburden | 4.85 | 5767 | 10951 | 96097 | 30645 | 7483 | 4103 | 30072 | 428 | 14 | 165 | 93 | 187 | 16 | 49 | 45 | 8 |
| 1-18-D Lignite | 5.15 | 718 | 1652 | 2512 | 233 | 6391 | 125 | 3552 | 43 | 4 | 6 | 4 | 79 | 1 | 25 | 20 | 17 |
| 1-19-D Lignite | 5.45 | 609 | 2208 | 7230 | 1000 | 6560 | 145 | 3724 | 63 | 3 | 24 | 10 | 108 | 4 | 24 | 18 | 27 |
| 1-20-D Overburden | 5.60 | 4485 | 11779 | 82608 | 1000 | 12364 | 3869 | 30382 | 471 | 14 | 134 | 75 | 424 | 14 | 67 | 47 | 2 |
| 1-21-D Lignite | 5.75 | 3510 | 6974 | 50912 | 21576 | 7039 | 2133 | 28376 | 314 | 11 | 158 | 92 | 242 | 13 | 64 | 37 | 44 |
| 1-22-D Overburden | 5.85 | 4900 | 10756 | 87974 | 1000 | 8418 | 3429 | 30294 | 499 | 14 | 151 | 106 | 387 | 19 | 96 | 46 | 7 |
| 1-23-D Overburden | 6.45 | 7708 | 9368 | 64715 | 19274 | 18107 | 3081 | 30374 | 395 | 13 | 106 | 119 | 436 | 15 | 50 | 38 | 11 |

*Height from base of major coal seam.

TABLE 3

(Continued)

| ID | Se | Br | Ru | Ag | Cd | Sb | Cs | Ba | La | Ce | Sm | Eu | Yb | Th | U |
|-------------------|----|----|-----|------|----|----|----|------|----|----|----|----|----|----|---|
| 1-1-D Underclay | 2 | 1 | 160 | 2.48 | 3 | 2 | 5 | 1132 | 27 | 53 | 3 | 1 | 1 | 10 | 4 |
| 1-2-D Lignite | 2 | 1 | 16 | 1.42 | 5 | 19 | 4 | 370 | 9 | 18 | 2 | 1 | 1 | 4 | 5 |
| 1-3-D Lignite | 1 | 3 | 5 | 0.83 | 5 | 5 | 1 | 185 | 3 | 9 | 2 | 0 | 0 | 1 | 6 |
| 1-4-D Lignite | 1 | 2 | 3 | 0.60 | 5 | 1 | 0 | 64 | 3 | 5 | 1 | 0 | 0 | 0 | 0 |
| 1-5-D Lignite | 1 | 2 | 3 | 0.71 | 5 | 0 | 0 | 39 | 3 | 4 | 0 | 0 | 0 | 1 | 1 |
| 1-6-D Lignite | 0 | 2 | 3 | 0.49 | 5 | 0 | 0 | 45 | 2 | 3 | 0 | 0 | 0 | 0 | 0 |
| 1-7-D Lignite | 1 | 3 | 3 | 0.67 | 4 | 1 | 0 | 66 | 4 | 6 | 1 | 0 | 0 | 1 | 2 |
| 1-8-D Lignite | 0 | 1 | 3 | 0.46 | 1 | 1 | 0 | 496 | 1 | 4 | 0 | 0 | 0 | 1 | 0 |
| 1-9-D Lignite | 1 | 1 | 5 | 1.12 | 9 | 5 | 1 | 114 | 4 | 8 | 2 | 0 | 1 | 11 | 4 |
| 1-10-D Lignite | 2 | 1 | 119 | 2.05 | 5 | 1 | 6 | 745 | 26 | 50 | 2 | 1 | 1 | 11 | 4 |
| 1-11-D Lignite | 1 | 4 | 6 | 1.44 | 7 | 4 | 0 | 266 | 5 | 9 | 2 | 0 | 1 | 3 | 4 |
| 1-12-D Overburden | 2 | 1 | 147 | 2.57 | 5 | 2 | 4 | 661 | 35 | 58 | 4 | 1 | 2 | 10 | 4 |
| 1-13-D Overburden | 2 | 3 | 107 | 2.19 | 5 | 1 | 3 | 673 | 31 | 60 | 3 | 1 | 2 | 11 | 2 |
| 1-14-D Overburden | 2 | 1 | 144 | 3.11 | 5 | 2 | 5 | 781 | 32 | 63 | 4 | 1 | 2 | 11 | 3 |
| 1-15-D Overburden | 9 | 3 | 46 | 7.14 | 20 | 0 | 0 | 595 | 23 | 6 | 3 | 1 | 3 | 3 | 3 |
| 1-16-D Lignite | 2 | 2 | 9 | 2.33 | 18 | 15 | 6 | 179 | 5 | 1 | 3 | 0 | 1 | 2 | 9 |
| 1-17-D Overburden | 2 | 1 | 138 | 2.00 | 5 | 2 | 1 | 761 | 32 | 56 | 3 | 1 | 2 | 10 | 3 |
| 1-18-D Lignite | 1 | 3 | 4 | 1.09 | 0 | 5 | 1 | 161 | 3 | 6 | 1 | 0 | 1 | 1 | 1 |
| 1-19-D Lignite | 1 | 3 | 4 | 1.00 | 4 | 4 | 1 | 95 | 2 | 4 | 1 | 0 | 0 | 2 | 3 |
| 1-20-D Overburden | 2 | 1 | 122 | 2.74 | 5 | 1 | 4 | 640 | 29 | 57 | 3 | 1 | 2 | 10 | 2 |
| 1-21-D Lignite | 4 | 3 | 66 | 2.21 | 8 | 8 | 4 | 559 | 10 | 36 | 3 | 1 | 2 | 8 | 5 |
| 1-22-D Overburden | 2 | 2 | 131 | 2.75 | 2 | 2 | 4 | 911 | 26 | 49 | 3 | 1 | 1 | 9 | 2 |
| 1-23-D Overburden | 1 | 2 | 90 | 2.30 | 5 | 2 | 2 | 691 | 29 | 55 | 3 | 1 | 2 | 9 | 2 |

*Height from base of major coal seam.

erals. The possible associations of trace and minor elements with clays are summarized by Finkelman (13). The elements which have possible affinities to clay and other sedimentary environments in relation to coal seams include Al, Sc, Ti, Cl, Cr, La, Mg, and Fe. A second group of elements, including Fe, Co, Ni, Zn, As, and Ag, may associate in the margins with pyrite or other sulfides. Uranium can be associated with the organic part of the coal but can be associated with a diverse suite of uranium minerals (13). Other elements, such as Ru, Ce, Sm, have not been extensively studied but appear to have an association with detrital minerals.

The elements which have an even distribution include Cd, Mn, Mg, Na, and Ca. As an example, Figure 4 represents the distribution of Ca within the stratigraphic sequence. The majority of these elements are organically bound or associated with authigenic minerals. The elements which are considered to be organically bound include Ca, Na, Mg, and Mn (14). This association would be as the counter ion with the carboxylic acid functional groups of the carbonaceous structure. Calcium, Mg, and Mn may also exist as carbonates which form in the coal during coalification. Calcite (CaCO_3), for example, was identified in the low-temperature ash of the coal. Cadmium in other coals has been found associated with sulfides (13). Its inclusion in this group may rather indicate an organic association, at least in this lignite. The calcium and cadmium ions have similar ionic potentials (~ 2) and may therefore behave similarly toward carboxylic groups.

Elements which showed a tendency to concentrate toward the base of the lignite seam are V, K, and Sb. Figure 5 represents this trend by a graph of the distribution of Sb. The increased concentration of K toward the base of the seam is very subtle. Vanadium and Sb increase sharply at the base of the seam. Vanadium has strong organic tendencies (13). Sb has strong chalcophile tendencies (15) so it is possible that Sb is associated with the sulfides.

The elements which reveal no clear pattern of distribution include Se, Br, Cs, Eu, and Yb. Bromine is an example, as illustrated in Figure 6. The probable reason is that low concentrations of these elements are near the detection limits of the analysis and thus may have greater experimental error.

Although the concentrations of rare earth elements are quite low, there is nevertheless a reasonable agreement with the rare earth abundance pattern in sedimentary rocks. This pattern can be seen in Table 4, which compares average concentrations in the main seam of lignite (samples 1-2-D through 1-11-D), after rejection of outliers, with the sedimentary rock pattern. For convenience in comparing the data, both sets of data have been calculated as ratios. The sedimentary rock data is from reference 16. Note that this comparison is only of the patterns of abundance, and not of the magnitudes. In the case of europium, the comparison is certainly influenced by working near the detection limit in the lignite samples.

TABLE 4
PATTERNS OF ABUNDANCE OF RARE EARTHS
IN LIGNITE AND SEDIMENTARY ROCKS

| Element | Lignite Ratio, La/x | Sedimentary Rock Ratio, La/X |
|---------|---------------------|------------------------------|
| La | 1.0 | 1.0 |
| Ce | 0.91 | 0.63 |
| Sm | 3.1 | 3.1 |
| Eu | 10 | 19 |
| Yb | 9.1 | 9.4 |

Reasonable qualitative agreement exists among the elemental variations observed here, the ionic potential of the elements, and the chemical fractionation behavior. Chemical fractionation determines the amount of each element present as ion-exchangeable cations, as acid-soluble minerals or coordination complexes, and as insoluble minerals. Our application of this procedure to other lignites has been discussed previously (17). In general, those elements which would be predicted to form insoluble hydrolysates on the basis of their ionic potential (that is, $3 < Z/r < 12$) are found concentrated near the margins of the seam and, in chemical fractionation, mainly occur as acid-insoluble minerals. Examples of elements in this category are Al, Ti, Cr, and Ni. On the other hand, elements of $Z/r < 3$ would likely exist as hydrated cations; these elements generally show even distribution through the seam and are removed by ion-exchange with ammonium acetate in chemical fractionation. Examples are Ca, Mg, and Na.

Variation Within the Overburden - The distribution of elements in the overburden is consistent in the clay-silt-sand regions with the exception of the concretion zone. This zone is extremely high in iron due to the siderite. The other elements which are concentrated in the concretion zone include Ag, Ni, Fe, Sc, Yb, Cd, Se, and Zn. The elements which are depleted are Co, Ce, Cs, As, Cr, Ru, Cl, and Na. The small coal seam directly above the concretion zone has high concentrations of As, V, Sb, and U. Figure 7 represents uranium distribution throughout the stratigraphic section, note that the highest concentration of uranium anywhere in the section is in the lignite seam directly above the concretion zone.

Many of the minor metallic elements have concentrations lying within 20% of the average values for shales. This comparison is illustrated by the data in Table 5, which compares the average concentrations in the underclay and overburden samples, after statistical rejection of outliers, with tabulated values from the literature (18). The most notable exception is manganese.

TABLE 5
COMPARISON OF AVERAGE MINOR ELEMENT CONCENTRATIONS FOR
OVERBURDEN/UNDERCLAY SAMPLES WITH AVERAGE CONCENTRATIONS FOR SHALES
CONCENTRATIONS IN PPM

| Element | Overburden/Underclay | Shales | Element | Overburden/Underclay | Shales |
|---------|----------------------|--------|---------|----------------------|--------|
| Ba | 760 | 600 | Sc | 15 | 15 |
| Ce | 56 | 70 | Th | 10 | 12 |
| Co | 13 | 20 | Ti | 3650 | 4600 |
| Cr | 92 | 100 | U | 2.8 | 3.5 |
| Mn | 269 | 850 | V | 139 | 130 |
| Ni | 72 | 80 | Zn | 51 | 90 |

The variation of potassium in the overburden and underclay is extreme, ranging from 1000 to 30,000 ppm. The reasons for this variability are not clearly understood, but may be due to the minerals in the overburden and underclay, some of which would be potassium-containing clays and others not. Figure 8 represents the distribution of potassium within the stratigraphic sequence.

INTERPRETATION OF PATTERNS OF ELEMENT DISTRIBUTION

The observed patterns of element distribution in the lignite seam may be explained by both changes in depositional conditions during accumulation and subsequent chemical changes during diagenesis and post-diagenetic processes. Depositional factors involving addition of greater fractions of detrital clay and silt at the beginning and end of peat deposition would increase Si, Al, Mg, Ca, Na, K, and possibly other elements in the margins of the lignite. Other possible depositional factors include changing of Eh or pH, influx of ash, or changing botanical factors at the beginning and end of peat deposition. Post-depositional factors related to the flow of meteoric water (i.e., water derived from the atmosphere) through the lignite laterally might selectively concentrate elements in the margins of the seam or at its center. Vertical flow might concentrate elements at either the upper or lower margin, depending on flow direction and on the nature of the adjoining sediments. Other post-depositional factors might be related to the changing geochemistry of the lignite-forming environment, such as Eh and pH changes, botanical changes due to breakdown of plant material, and geological factors such as depth of burial, temperature, compaction, or changes in groundwater chemistry. The existence of several types of patterns suggests that several processes have been operative during the geological history of this sequence.

Future work will include a very detailed sampling of several vertical sections of a mine to describe groundwater influences on the formation of authigenic minerals and on the distribution or organically associated elements.

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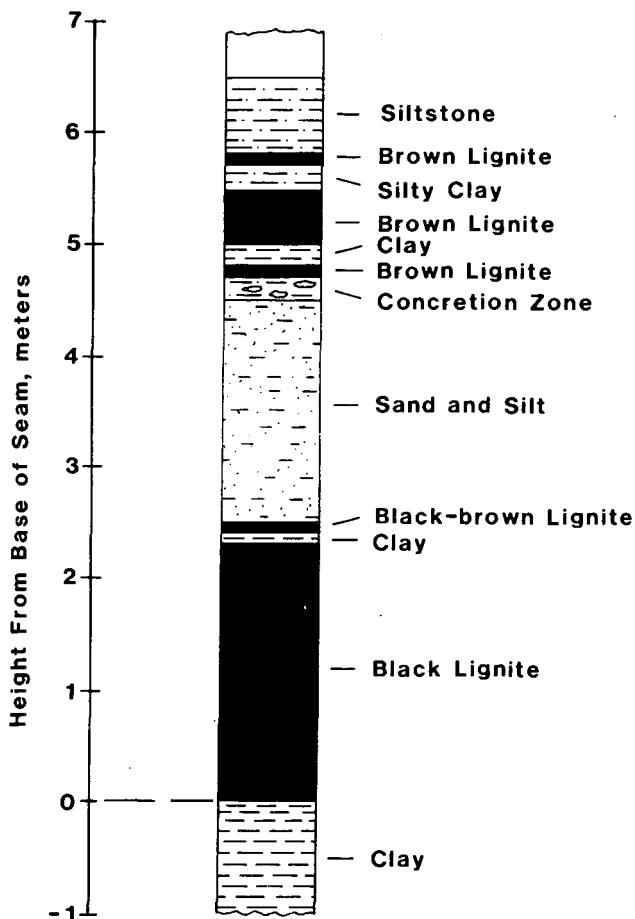
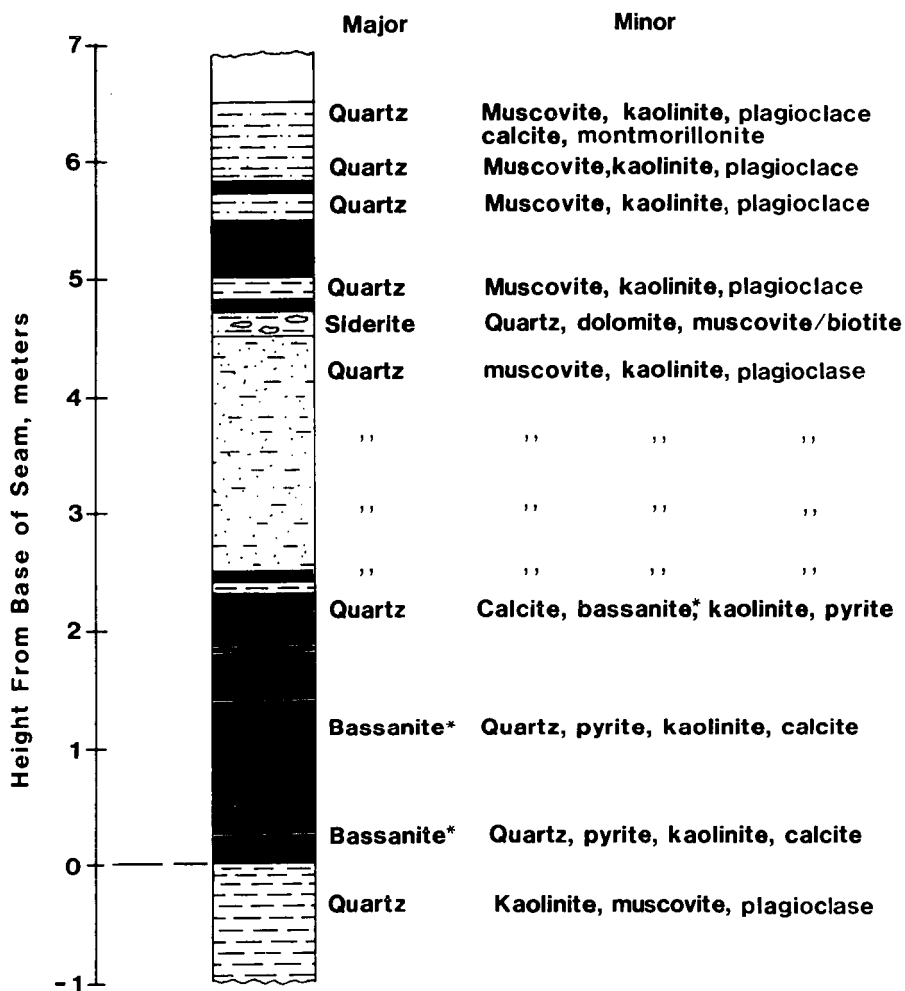


FIGURE 1. Description of stratigraphic sequence.

X-ray diffraction mineral identification⁺



⁺Abundance listed in decreasing order

*Bassanite may be a product of the Low-temperature ashing procedure

FIGURE 2. Mineralogy of the stratigraphic sequence.

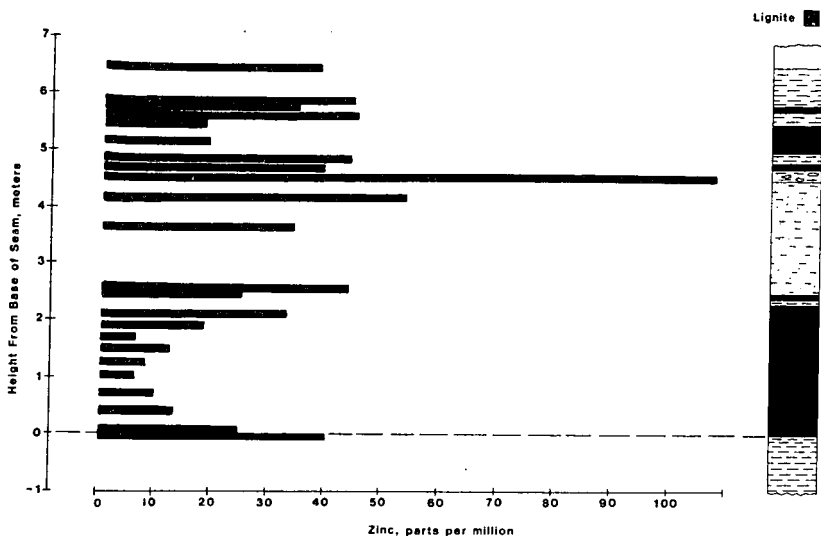


FIGURE 3. Zinc distribution in the stratigraphic sequence.

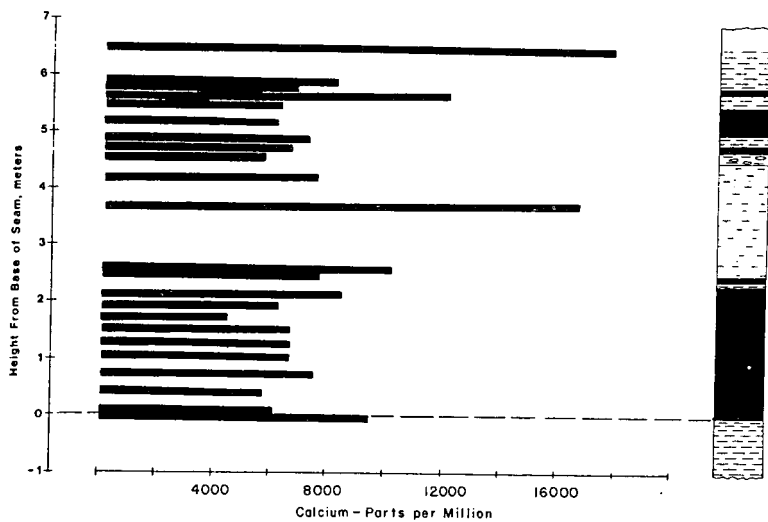


FIGURE 4. Calcium distribution in the stratigraphic sequence.

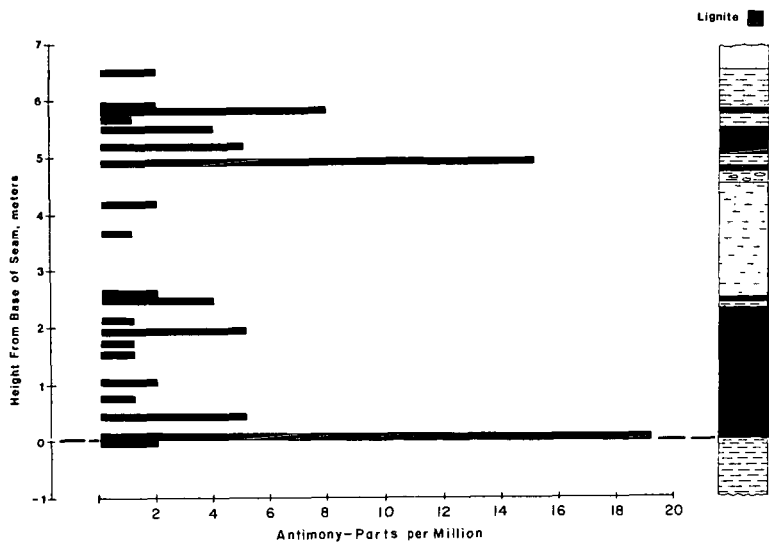


FIGURE 5. Antimony distribution in the stratigraphic sequence.

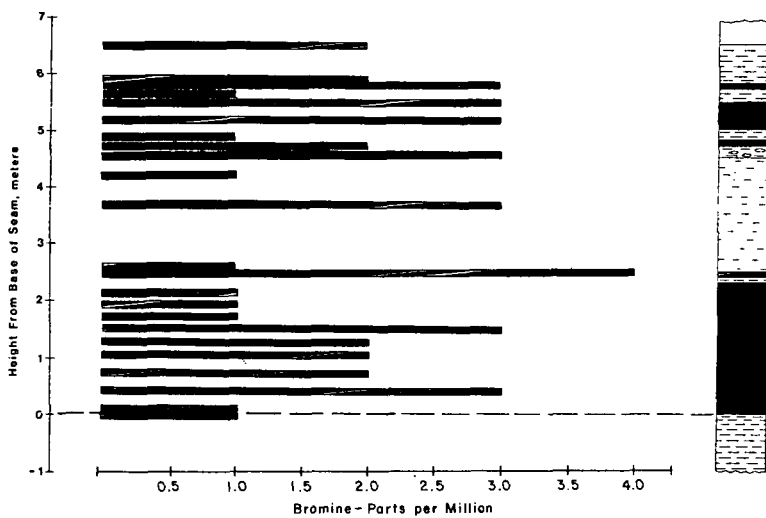


FIGURE 6. Bromine distribution in stratigraphic sequence.

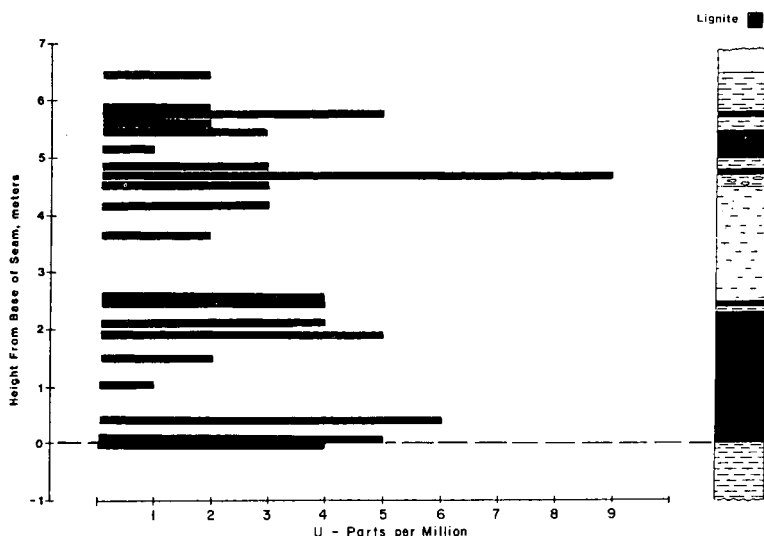


FIGURE 7. Uranium distribution in the stratigraphic sequence.

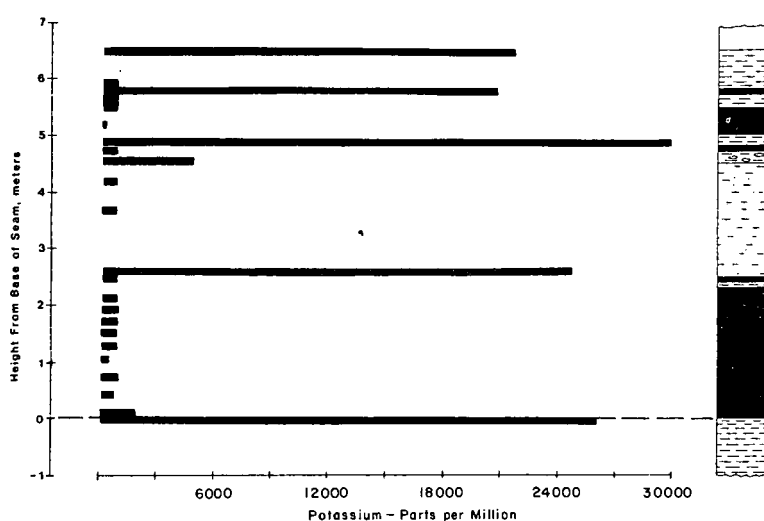


FIGURE 8. Potassium distribution in the stratigraphic sequence.